

AQUEOUS COLLOIDAL SUSPENSION OF THE HYDROXIDE OF AT LEAST
ONE TRANSITION ELEMENT, FOR THE PURPOSE OF THE REDUCTION
OF CHROMIUM IN CEMENT

The invention relates to an aqueous colloidal suspension of the hydroxide of at least one transition element whose oxidation-reduction potential is less than that of the $\text{CrO}_7^{2-}/\text{CrO}_4^{2-}$ couple (-0.12 V) with a pH
5 between 2 and 11, limits excluded, and containing less than 0.02% of soluble ions of at least one transition element in solution, the suspension being designed to reduce the chromium VI content of cement to a value at most equal to 2 ppm.

10 The invention more particularly relates to an aqueous suspension of tin hydroxide with an oxidation-reduction potential of -0.96 V, of iron hydroxide with an oxidation-reduction potential of -0.56 V, of manganese hydroxide with an oxidation-reduction potential of -0.4 V,
15 implemented alone or as a mixture, with a pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of cement to a value at most equal to 2 ppm, the suspension being stabilised by means of a stabilisation agent.

The invention also relates to the use of aqueous suspensions of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of cement during the process of preparation of the cement to form a treated cement whose chromium VI content has a value at most equal to 2 ppm.

The invention finally relates to a process for treatment of cements to reduce the chromium VI content of the cement to a value at most equal to 2 ppm.

It is known that cements contain chromium compounds which, when the cements are mixed with water, appear in the form of chromium VI dissolved in water. Now, chromium VI soluble in the water of the cements may be the origin of allergic reactions for persons who come in contact with products containing hydrosoluble compounds of hexavalent chromium. Chromium is even suspected of being carcinogenic for the human. Thus, construction workers whose skin, in general the hands and the arms, is brought in regular contact with mixtures of cement and water are capable of contracting contact eczema due to the too-elevated chromium VI content of the cements.

Systems exist in the state of the art that are designed to reduce hydrosoluble hexavalent chromium compounds in the cements. It is known for example that the addition of ferrous sulphate reduces the content of chromium dissolved in a cement-water mixture. The ferrous sulphate can, for example, be added during the preparation of mixtures containing cement or during the manufacture of the cement. Iron (II) sulphate reduces Cr^{6+} to Cr^{3+} , which has low solubility in the cement-water mixtures. Thus, the reaction between the Fe^{2+} and Cr^{6+}

ions takes place in aqueous medium, i.e. when the water is added to the cement containing iron (II) sulphate.

Since the nineteen-seventies, cement manufacturers have been performing a ferrous sulphate treatment in particular at the time of the grinding step in order to reduce the chromium VI content in the cements and thus limit the risks of eczema being contracted by construction workers in regular contact with cement-water mixtures. However, this ferrous sulphate treatment of cements that makes it possible to reduce the chromium VI content of the treated cements turns out to be rather ineffective and presents numerous disadvantages.

As a matter of fact, it turns out to be necessary in practice to use iron sulphate in powder form in order to obtain reduction of chromium (VI) to chromium (III) with iron (II) ions. Now, oxygen in the air can convert iron (II) to iron (III). For this reason, particular attention as well as particular implementation conditions prove indispensable.

Other reduction pathways of chromium (VI) have been developed, as for example the reduction of chromium (VI) by organic systems such as aldehydes, and heterocyclic compounds such as, for example, pyridine. But use of these organic systems in practice has proven maladapted for economic reasons connected in particular to the low stability of these organic systems in the preparations of cement or to the quantities to be used. It is known, moreover, in the state of the art that a solution of soluble Sn^{2+} ions makes it possible to reduce chromium VI.

There is, therefore, in the state of the art, no aqueous suspension with a base of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2

and 11, limits excluded, capable of reducing the chromium VI content of cement, cumulatively fulfilling the following conditions:

- high stability, even in concentrated suspension,
- 5 - viscosity of the suspensions constant over time and which remains low,
- viscosity in concentrated solution sufficiently low so as to facilitate their use,
- formulation at a pH between 2 and 11, limits excluded,
- 10 to facilitate storage, transport and conditions of implementation.

Surprisingly, it was found that an aqueous suspension of the hydroxide of at least one transition element, in particular of tin hydroxide and/or iron hydroxide and/or manganese hydroxide with a pH between 2 and 11, limits excluded, reduces the chromium VI content of the cement to a value at most equal to 2ppm and is characterised in that it comprises from 0.5 to 80% by weight of dry matter of the hydroxide of at least one transition element, in particular of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide with respect to the quantity of water, the hydroxide being implemented alone or as a mixture and in that it is stabilised by a hydrosoluble stabilisation agent.

Consequently, this invention also has for object the use of these aqueous suspensions of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of the cement in order to produce cements whose chromium VI content is at most equal to 2 ppm, designated below as treated cements.

This invention also relates to a process for treatment of cements to reduce the chromium VI content of the cement to a value at most equal to 2 ppm, which is characterised in that, after the step of calcination of the clinker in the cement manufacturing process, an aqueous suspension is introduced, of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide with a pH between 2 and 11, limits excluded, the suspension being as previously defined, according to the invention to fabricate cements whose chrome VI content is at most equal to 2 ppm, designated below as treated cements.

This invention also concerns the use of treated cement produced according to the treatment process of the invention and of which the chromium VI content is at most equal to 2 ppm in order to prepare a concrete composition comprising treated cement, water and the customary components.

The invention relates finally to compositions of concrete comprising cement, water and the customary components and being characterised in that, at the time of the mixing of the various components an aqueous suspension of tin hydroxide of pH between 2 and 11, limits excluded, is added, as defined within the framework of the invention in a quantity sufficient to reduce the soluble chromium VI content to a value at most equal to 2 mg of Cr(VI) per kg of cement.

The chromium ions present the characteristic of having a strong oxidizing action. Thus, in the presence of oxidisable substances, chromium (VI) is reduced to chromium (III). The chemical reaction of oxidation-reduction which describes this mechanism is defined as the transfer of electrons from the reduced form red_2 of a

redox couple (ox_2/red_2) to the oxidized form ox_1 of another redox couple (ox_1/red_1). It can take place only if the oxidation-reduction potential of the couple ox_1/red_1 is greater than the oxidation-reduction potential of the couple ox_2/red_2 .

When the couples are classified on a scale of redox potential, this transfer obeys a law called the law of gamma (figure 2).

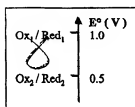
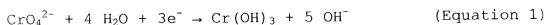


Figure 2: Law of gamma

It is then appropriate within the framework of the invention to select the redox couples involved in the case of the reduction of chromium VI in the cement. In order to do so, it appears necessary to determine in which ionic form the chromium is present in the interstitial medium of the cement so as to be able to select the couples capable of reducing chromium in the interstitial medium of the cement.

This interstitial medium of the cement presents a strongly basic pH greater than 11 and in such a medium, chromium VI is present in the CrO_4^{2-} form.

Consequently, the oxidation-reduction couple involved appears to be $CrO_4^{2-}/Cr(OH)_3$ and the equation of the reduction associated with this couple is:



The verified oxidation-reduction potential of the $\text{CrO}_4^{2-} / \text{Cr}(\text{OH})_3$ couple is -0.12 V and an oxidation-reduction reaction with another ox/red couple can take place only if this other ox/red couple presents an oxidation-reduction potential less than -0.12 V .

According to the invention, in the case of the tin hydroxide selected, the $\text{Sn}(\text{OH})_6^{2-} / \text{Sn}(\text{OH})_4^{2-}$ couple possesses a measured oxidation-reduction potential of -0.96 V , less than that of the $\text{CrO}_4^{2-} / \text{Cr}(\text{OH})_3$ couple which is -0.12 V .

Consequently, the ox/red couple selected observes the following oxidation-reduction equations and the corresponding transfer of electrons takes place according to the abovementioned law of gamma (Figure 3):

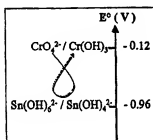
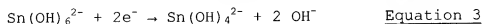
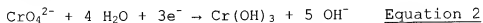
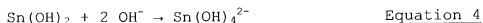


Figure 3

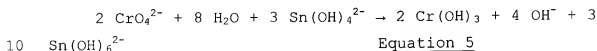


At the time of the application of the selected ox/red couple, in the interstitial medium of the cement, tin hydroxide $\text{Sn}(\text{OH})_2$ reacts with the hydroxide ions of the medium to form the $\text{Sn}(\text{OH})_4^{2-}$ ion according to equation 4.



The $\text{Sn}(\text{OH})_4^{2-}$ ion is the reduced form of the $\text{Sn}(\text{OH})_6^{2-}$ / $\text{Sn}(\text{OH})_4^{2-}$ couple. This ox/red couple possesses a potential of -0.96 V.

According to the law of gamma for the couples CrO_4^{2-} / $\text{Cr}(\text{OH})_3$ and $\text{Sn}(\text{OH})_6^{2-}$ / $\text{Sn}(\text{OH})_4^{2-}$ (Figure 3), $\text{Sn}(\text{OH})_4^{2-}$ reduces the CrO_4^{2-} ion to $\text{Cr}(\text{OH})_3$ according to the following oxidation-reduction reaction (Equation 5).



As opposed to, and as shown in figure 3, the law of gamma for the CrO_4^{2-} / $\text{Cr}(\text{OH})_3$ couple (-0.12 V), implementation of an Sn^{4+} / Sn^{2+} couple of oxidation-reduction potential equal to $+0.15$ V appears to be unable to be used as a reducer of chrome VI in the interstitial medium of the cement: this couple in fact has an oxidation-reduction potential greater than that of the CrO_4^{2-} / $\text{Cr}(\text{OH})_3$ couple in the scale of oxidation-reduction potentials and consequently the oxidation-reduction reaction between Sn^{2+} and CrO_4^{2-} , the species present in said interstitial medium of the cement, cannot take place as shown by figure 4 below.

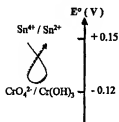


Figure 4

According to the invention, in the case of the selection of iron hydroxide, the $\text{Fe}(\text{OH})_3$ / $\text{Fe}(\text{OH})_2$ couple possesses a measured oxidation-reduction potential of -

0.56 V, less than that of the $\text{CrO}_4^{2-} / \text{Cr(OH)}_3$ couple which is -0.12 V.

Consequently, the oxidation-reduction equations are the following and the corresponding transfer of electrons takes place according to the following law of gamma (figure 5):

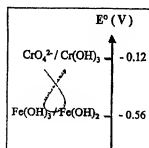
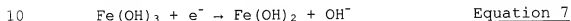
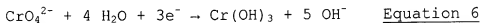
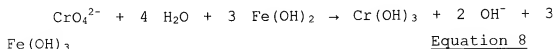


Figure 5



During the application of the ox/red couple selected, in the interstitial medium of the cement, the $\text{Fe(OH)}_3 / \text{Fe(OH)}_2$ couple reduces the CrO_4^{2-} ion to Cr(OH)_3 , according to the oxidation-reduction reaction described below (equation 8).



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According to the invention, in the case of the selection of manganese hydroxide, the $\text{Mn(OH)}_3 / \text{Mn(OH)}_2$ couple possesses a measured oxidation-reduction potential of -0.40 V, less than that of the $\text{CrO}_4^{2-} / \text{Cr(OH)}_3$ couple, which is equal to -0.12 V.

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Consequently, the oxidation-reduction equations are the following and the corresponding transfer of electrons takes place according to the law of gamma (figure 6):

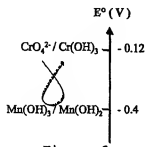
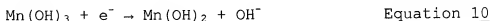
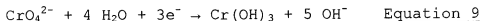
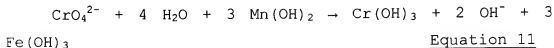


Figure 6



During the application of the selected red/ox couple in the interstitial medium of the cement, the manganese hydroxide Mn(OH)_3 / Mn(OH)_2 reduces the CrO_4^{2-} ion to Cr(OH)_3 according to the following oxidation-reduction reaction (equation 11).



Thus the aqueous suspension of tin hydroxide and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, according to the invention is prepared, respectively, from a stannous compound, a ferrous compound, or a manganous compound in the presence of a strong base. In order to do this, a suspension of tin hydroxide can be prepared, of pH between 2 and 11, exclusive of limits, from a stannous compound and sodium hydroxide. Among the stannous compounds, it is possible

to cite, by way of example, the tin chlorides, the tin sulphates and other stannous compounds routinely used and easily dissociated in aqueous media.

In the same way, a suspension of iron hydroxide can
5 be prepared, of pH between 2 and 11, exclusive of limits, from a ferrous compound and sodium hydroxide.

Among the ferrous compounds, it is possible to cite, by way of example, the iron chlorides, the iron sulphates and other ferrous compounds routinely used and easily
10 dissociated in aqueous media.

Finally, a suspension of manganese hydroxide can be prepared, of pH between 2 and 11, exclusive of limits, from a manganous compound and sodium hydroxide. Among the manganous compounds, it is possible to cite, by way of
15 example, the manganese chlorides, the manganese sulphates and other manganese compounds routinely used and easily dissociated in aqueous media.

The aqueous suspension of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and
20 11, limits excluded, thus obtained appears in the form of a colloidal suspension which tends to sediment. This is why a homogenisation by stabilisation of the aqueous colloidal suspension of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and
25 11, limits excluded, is done through implementation of a hydrosoluble stabilisation agent. This agent for stabilisation of said suspension proves to be indispensable for the production of an aqueous suspension of tin hydroxide, and/or iron hydroxide and/or manganese
30 hydroxide, of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of the cement to a value at most equal to 2 ppm, comprising from 0.5 to

80% by weight of dry matter of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide with respect to the quantity of water, so that said aqueous suspension may be used on an industrial scale.

5 An aqueous suspension of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide as defined according to the invention may preferentially comprise from 5 to 70% by weight of dry matter of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide with respect to the
10 quantity of water, and more preferentially from 10 to 60% by weight of dry matter of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide with respect to the quantity of water.

As specified previously, the suspension according to
15 the invention is stabilised by a hydrosoluble stabilisation agent.

By hydrosoluble stabilisation agent, we understand in this exposition a hydrosoluble dispersing agent of molar mass less than 100,000 g/mol.

20 According to the invention, the hydrosoluble agent which is a dispersing agent, is preferentially chosen from among the polynaphthalene sulfonates, the polyoxyalkylene phosphonates, preferentially di-phosphonates and polyoxyalkylene polycarboxylates of
25 molar mass less than 100,000 g/mol.

By way of polyoxyalkylene polycarboxylates defined as dispersing agents according to the invention, it is possible to cite, for example, copolymers of the polycarboxylic type obtained by polymerisation of a
30 polyalkyleneglycol monoester monomer containing from 2 to 300 molecules of oxyalkylene with at least one monomer chosen from among the unsaturated monocarboxylic acids

such as acrylic acid, methacrylic acid, and the unsaturated dicarboxylic acids, such as maleic anhydride. By way of examples, it is possible to cite (meth)acrylate copolymers with a polyalkylene glycol chain containing
5 from 2 to 300 molecules of oxyalkylene, maleate copolymers with a polyalkylene glycol chain containing from 2 to 300 molecules of oxyalkylene, more preferentially (meth)acrylate copolymers with a polyalkylene glycol chain containing from 2 to 300
10 molecules of oxyalkylene in C₂-C₃.

By way of polyoxyalkylene phosphonates, used as dispersing agents according to the invention, it is possible to preferentially cite the polyoxyethylene di-phosphonates.

15 The introduction of thickeners into the aqueous suspensions in order to make possible adjustment of their viscosity is known from the state of the art. Thus, aqueous suspensions of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide according to the
20 invention may possibly include a thickening agent enabling an adjustment of viscosity.

By way of thickening agent, it is possible to cite hydrosoluble polymers of molar mass greater than 10⁶ g/mol.

25 By way of examples of thickening agents, it is possible to cite for example the xanthane, welan, carouba and guar gums, the celluloses and their derivatives or the polyethylenes, the polyacrylates and their derivatives of molar mass greater than 10⁶ g/mol.

30 Thus an aqueous suspension of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, capable of reducing the chromium

VI content of the cement, presents quite cumulatively the following criteria:

- high stability, even in concentrated solution,
 - viscosity of the suspensions that is constant over time
- 5 and which remains low,
- viscosity in concentrated solution sufficiently low so as to facilitate their use, and
 - packaging at a pH between 2 and 11, limits excluded, to facilitate storage, transport and conditions of
- 10 implementation, and more preferably packaging in compliance with standards of hygiene and safety with which cement manufacturers are confronted, in particular as regards aspects connected with the corrosive character of products at pH close to 1.

15 Consequently, aqueous suspensions of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of the cement according to the invention may be used to produce cements whose chromium

20 VI content is at most equal to 2 ppm.

The treatment process for cements implementing aqueous suspensions of tin hydroxide of pH between 2 and 11, limits excluded, according to the invention is carried out during the cement manufacturing step in the

25 cement factory. This treatment process consists in the introduction, after the clinker calcination step during the cement manufacturing process, of an aqueous suspension of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide with a pH between 2 and 11, limits

30 excluded, of the invention to reduce the chromium VI content of the cements to a value at most equal to 2 ppm

and thus to obtain cements whose chromium VI content is at most equal to 2 ppm.

Example 1:

- 5 A suspension of tin hydroxide is prepared from a source of tin which can be tin chloride or tin sulphate according to the following protocol which comprises:
- definition of the proportions between an alkaline agent which is an aqueous solution of sodium hydroxide (NaOH-N)
 - 10 and the tin source in order to transform this tin source into tin hydroxide $[\text{Sn}(\text{OH})_2]$;
 - introduction of the tin source into the aqueous solution of sodium hydroxide in a slow and regular fashion, in order to avoid dismutation of the tin.
- 15 Consequently we observe:
- the appearance of a white-yellow precipitate of $\text{Sn}(\text{OH})_2$;
 - a phenomenon of rapid decantation of the $\text{Sn}(\text{OH})_2$ precipitate revealing that an aqueous suspension of said $\text{Sn}(\text{OH})_2$ cannot be stable.
- 20 In order to create a stable suspension of tin hydroxide in its aqueous precipitation medium, a dispersing agent is implemented from a suspension of tin hydroxide of 30% concentration with respect to the quantity of water.
- 25 Three trials were made with the three dispersing agents set forth below:
- 1st trial: the dispersing agent is polynaphthalene sulfonate;
 - 2nd trial: the dispersing agent is polyoxyethylene di-
 - 30 phosphonate;
 - 3rd trial: the dispersing agent is a polycarboxylate of polyoxyethylene.

In each trial, the concentration of dispersing agent is 2% by weight with respect to the suspension of tin hydroxide at a concentration of 30%.

5 In the three trials thus performed, the resulting suspension of tin hydroxide manifests a certain stability since it appears with a milky appearance; however, the beginning of decantation may manifest after several hours of sitting.

These three suspensions of tin hydroxide were then treated with a thickening agent:

- the first trial received Xanthane gum in the proportion of 0.4% by weight with respect to the suspension of sodium hydroxide. After this treatment, the pH of the treated suspension is 2.5;
- 15 - trials 2 and 3 received a mixture of Xanthane gum and polyoxyethylene of high molar mass in the proportion of 2% by weight in water. After treatment, the pH of the treated suspension is 2.5.

These three suspensions of $\text{Sn}(\text{OH})_2$, containing the dispersing agent and a thickening agent, showed excellent stability over time: no decantation is visible after several days of sitting.

The use of such suspensions of $\text{Sn}(\text{OH})_2$ at various concentrations makes it possible to significantly reduce the chromium VI concentration in the cements.

25 The filtrates from suspensions of cement ground, on the one hand, without additives and ground, on the other hand, while increasing the stannous concentration were analysed by ICP (Inductively Coupled Plasma) after hydration in water. The assay of total chromium is obtained by this technique, i.e. the chromium (VI) ions and the chromium (III) ions taken together, the latter

being very insoluble in water. The results obtained are shown in figure 1.

The untreated cement presents 10.5 ppm of chromium VI ions.

- 5 After treatment of the cement by the suspension of Sn(OH)_2 according to the invention in the proportion of at least 300 ppm of Sn^{2+} , the chromium VI content of the cement is strictly less than 2 ppm.

10 Example 2:

A suspension of tin hydroxide is prepared from a tin source which can be tin chloride or tin sulphate according to the protocol which comprises the following steps:

- 15 - definition of the proportions between an alkaline agent which is an aqueous solution of sodium hydroxide (NaOH-N) and the tin source in order to transform this tin source into tin hydroxide $[\text{Sn(OH)}_2]$ and obtain an aqueous suspension of tin hydroxide charged at 15% by weight in
- 20 said hydroxide,
- introduction of the tin source into the aqueous sodium hydroxide solution in a slow and regular fashion, in order to avoid dismutation of the tin,
- the appearance of a white-yellow precipitate of Sn(OH)_2 ;
- 25 - the appearance of a phenomenon of rapid decantation of the Sn(OH)_2 precipitate showing that an aqueous suspension of said Sn(OH)_2 cannot be stable in this state,
- the creation of a stable suspension of tin hydroxide in its aqueous precipitation medium, by implementation of a
- 30 dispersing agent, starting from a suspension of tin hydroxide at 15% concentration with respect to the quantity of water.

Six trials numbered 4 to 9 were conducted with:

- the same reducing agent, which is tin hydroxide in suspension in water
- three types of dispersing agents implemented in the aqueous suspension of tin hydroxide
- three types of thickening agents implemented in the aqueous suspension of tin hydroxide
- quantities of aqueous suspensions of tin hydroxide expressed as ppm which can be different according to the trials.

These six suspensions of Sn(OH)_2 , containing the dispersing agent and a thickening agent, showed excellent stability over time: no decantation is visible after several days of sitting.

- The use of such Sn(OH)_2 suspensions at different concentrations makes it possible to drastically reduce the chromium VI concentration in the cements.

- The filtrates from suspensions of cement ground, on the one hand, without additive and, on the other hand, ground while increasing the stannous concentration were analysed by ICP (Inductively Coupled Plasma) after hydration in water. The assay of total chromium is obtained by this technique, i.e. the chromium (VI) ions and the chromium (III) ions taken together, the latter being very insoluble in water. The operatory conditions of trials four to nine and the results obtained are brought together in table 1 below.

- The untreated cement presents, according to trials four to nine, a quantity of chromium VI ions between 6 and 6.2 ppm.

After treatment of the cement by the suspensions of Sn(OH)_2 according to the invention in the proportion of

at least 300 ppm of Sn^{2+} , the chromium VI content of the cement is between 0.1 and 0.2 ppm and consequently strictly less than 2 ppm.

Table 1:

Trial No.	Nature of reducing agent implemented in the suspension	Nature of the dispersing agent	Concentration of dispersing agent in % by weight	Nature of thickener	Concentration of thickener in % by weight	Stability of suspension	Chromium VI content of cement before treatment in ppm	Quantity of suspension introduced into cement in ppm	Chromium VI content of cement after treatment in ppm
4	15% tin hydroxide	Polyacrylate	1.4	Xanthane gum, polyoxyethylene	2 %	Good	6	3000	0.1
5	15% tin hydroxide	Polyphosphonate	1.4	Xanthane gum, polyoxyethylene	2 %	Good	6	3000	0.2
6	15% tin hydroxide	Polyoxyethylene Polycarboxylate	1.4	Xanthane gum	0.4 %	Very good	6.2	3000	0.1
7	15% tin hydroxide	Polyoxyethylene Polycarboxylate	1.4	Guar gum Tylose	0.3 % 0.2 %	Very good	6.2	3000	0.1
8	15% tin hydroxide	Polyoxyethylene Polycarboxylate	1.4	Xanthane gum	0.4 %	Very good	6.1	2000	0.1
9	15% tin hydroxide	Polyoxyethylene Polycarboxylate	1.4	Xanthane gum	0.4 %	Very good	6.1	1500	0.2

Thus treatment of the cement according to the invention appears particularly effective since the chromium VI content after treatment, which is between 0.1 and 0.2 ppm appears to always be very much less than the upper limit imposed of 2 ppm.

Example 3:

Aqueous suspensions of the hydroxides of tin, iron and manganese were prepared from sources of these various elements, which can be salts such as chlorides, sulphates or other salts, following the preparation protocol comprising the following steps:

- definition of the proportions between an alkaline agent which is an aqueous solution of sodium hydroxide (NaOH-N) and the source of tin, iron, or manganese in order to transform these sources into the hydroxide of tin, iron, or manganese;
- introduction of the source of tin, iron and manganese into the aqueous solution of sodium hydroxide in a slow and regular fashion, in order to avoid in particular the dismutation of the element implemented,
- the appearance of a precipitate,
- the appearance of a phenomenon of rapid decantation of the precipitated hydroxide showing that the aqueous

- different reducing agents which are a mixture of tin hydroxide and iron hydroxide, of iron hydroxide alone and of manganese hydroxide alone,
- the same type of dispersing agent,
- 5 - the same type of thickening agent,
- quantities of aqueous hydroxide suspensions expressed in ppm which are identical for these three trials.

These three suspensions of reducing agents of Cr VI containing a dispersing agent and a thickening agent,
10 showed excellent stability over time: no decantation is visible after several days of sitting.

Use of these suspensions at various concentrations makes it possible to significantly reduce the chromium VI concentration in the cements.

- 15 The filtrates from suspensions of cement ground, on the one hand, without additive and, on the other hand, ground in the presence of the reducing agent were analysed by ICP (Inductively Coupled Plasma) after hydration in water. The assay of total chromium is
20 obtained by this technique, i.e. chromium (VI) ions and chromium (III) ions taken together, the latter being very insoluble in water. The operatory conditions for trials 10, 11 and 12 and the results obtained are presented in table 2 below.

Table 2:

trial No.	Nature of the reducing agent implemented in the suspension	Nature of the dispersing agent	Concentration of the dispersing agent in % by weight	Nature of the thickener	Concentration of the thickener in % by weight	Suspension stability	Cr content of the cement before treatment in ppm	Quantity of suspension introduced into cement in ppm	Cr content of the cement after treatment in ppm
10	10% tin hydroxide, 20% iron hydroxide	Polyoxyethylene polycarboxylate	1.4	Xanthane gum	0.4%	Good	6.2	3000	0.1
11	20% Iron hydroxide	Polyoxyethylene polycarboxylate	1.4	Xanthane gum	0.4%	Very good	6.1	3000	0.1
12	15% manganese hydroxide	Polyoxyethylene polycarboxylate	1.4	Xanthane gum	0.4%	Very good	6.1	3000	1.2

5 Thus treatment of the cement according to the invention appears particularly effective since the chromium VI content after treatment which is between 0.1 and 1.2 ppm appears to always be less than the imposed upper limit of 2 ppm.

CLAIMS

1. Aqueous suspension of the hydroxide of at least one selected transition element, whose oxidation-reduction potential is less than that of the $\text{CrO}_7^{2-} / \text{CrO}_4^{2-}$ couple with a pH between 2 and 11, limits excluded, to reduce
5 the chromium VI content of cement to a value at most equal to 2 ppm, characterised in that it includes from 0.5 to 80% by weight of dry matter of the hydroxide of at least one transition element with respect to the quantity of water and in that it is stabilised by a hydrosoluble
10 stabilisation agent.

2. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 1, characterised in that it preferentially includes from 5 to 70% by
15 weight of dry matter of the hydroxide of at least one transition element with respect to the quantity of water, and more preferentially from 10 to 60% by weight of dry matter of the hydroxide of at least one transition element with respect to the quantity of water.

20 3. Aqueous suspension of the hydroxide of at least one transition element as claimed in one or the other of claims 1 and 2, characterised in that the hydroxides of the transition elements are chosen from the group formed
25 by tin hydroxide, iron hydroxide and manganese hydroxide, taken alone or in a mixture.

4. Aqueous suspension of the hydroxide of at least one transition element as claimed in any of the preceding
30 claims, characterised in that the hydrosoluble

stabilisation agent is a dispersing agent of molar mass less than 100,000 g/mol.

5 5. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 4, characterised in that the dispersing agent is chosen from the group made up by the polynaphthalene sulfonates, the polyoxyalkylene di-phosphonates and the polyoxyalkylene polycarboxylates.

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6. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 5, characterised in that the dispersing agent is chosen from among the polynaphthalene sulfonates of molar mass less than 15 100,000 g/mol.

7. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 5, characterised in that the dispersing agent is chosen from among 20 copolymers of the polycarboxylic type obtained by polymerisation of a polyalkyleneglycol monoester monomer containing from 2 to 300 molecules of oxyalkylene with at least one monomer chosen from among the unsaturated monocarboxylic acids and the unsaturated dicarboxylic 25 acids.

8. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 7, characterised in that the dispersing agent is chosen from among 30 (meth)acrylate copolymers with a polyoxyalkylene polyalkylene glycol chain containing from 2 to 300 molecules of oxyalkylene.

9. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 5, characterised in that the dispersing agent is chosen from among the
5 polyoxyalkylene di-phosphonates, and preferentially the polyoxyethylene di-phosphonates.

10. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 1, characterised
10 in that it also includes an agent for adjustment of the viscosity of said suspension.

11. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 10, characterised
15 in that the agent for adjustment of viscosity is chosen from among hydrosoluble polymers of molar mass greater than 10^6 g/mol.

12. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 11, characterised
20 in that the agent for adjustment of viscosity is chosen from the group made up by the xanthane, welan, carouba and guar gums, the celluloses and their derivatives.

25 13. Aqueous suspension of the hydroxide of at least one transition element as claimed in claim 11, characterised in that the agent for adjustment of viscosity is a hydrosoluble polymer of molar mass greater than 10^6 g/mol
30 chosen from among the polyethylenes, the polyacrylates and their derivatives.

14. Aqueous suspension of the hydroxide of at least one transition element as claimed in any of the preceding claims, characterised in that it presents a pH precisely between 2 and 11, limits excluded.

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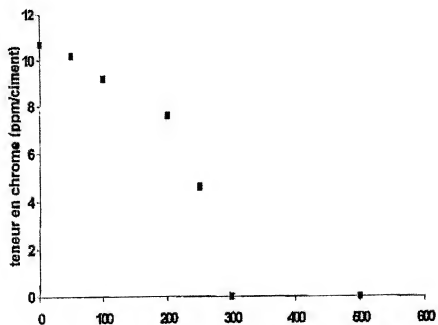
15. Use of aqueous suspensions of the hydroxide of at least one transition element of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of cement as claimed in claim 1 to produce
10 cements whose chromium VI content is at most equal to 2 ppm.

16. Process for treatment of cements, characterised in that introduction is made, after the clinker calcination
15 step during the cement preparation process the cement, of an aqueous suspension of the hydroxide of at least one transition element with a pH between 2 and 11, limits excluded, as defined in claim 1 to reduce the chromium VI content of the cements to a value at most equal to 2 ppm
20 and produce cements whose chromium VI content is at most equal to 2 ppm.

17. Use of cement produced by the process for treatment of cements as claimed in claim 11 and whose chromium VI
25 content is at most equal to 2 ppm to prepare a concrete composition comprising treated cement, water and the usual components.

18. Concrete compositions comprising cement, water and
30 the usual components, characterised in that at the time of mixture of the various components, addition is made of an aqueous suspension of the hydroxide of at least one

transition element, of pH between 2 and 11, limits excluded, as defined in claim 1, in sufficient quantity to reduce the soluble chromium VI content to a value at most equal to 2 ppm of Cr(VI).

Figure 1Assay of Cr VI: Frangay cement

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Quantity of tin (ppm/cement)

Ordinate: "chromium content (ppm/cement)"